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THE EFFECT OF QUARTZ-PYROPHYLLITE RAW MATERIAL ON PORCELAIN STRUCTURE FORMATION

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An integrated study of the physicochemical properties and behavior in firing of quartz-pyrophyllite material demonstrated its suitability for use in the composition of porcelain mixtures as a substitute for quartz and partly kaolin. The household porcelain obtained is characterized by a low firing temperature (1280 – 1300°C) and good physicomachanical properties.

The compositions of porcelain mixtures can contain not only traditional but also non-traditional raw materials [1 – 3]. Quartz-pyrophyllite rocks known as “porcelain stone” are hydrothermally modified rocks with a fine-grained structure and chemical and mineralogical composition favorable for the production of fine ceramic mixtures.

The present study investigated quartz-pyrophyllite rocks of the Bainaksaiskoe deposit (Republic of Uzbekistan) with the purpose of producing household porcelain products.

The petrographic study of the quartz-pyrophyllite material revealed that the rock is composed of solid scaly aggregates with silken matte luster. The main mineral of the rock is pyrophyllite in the form of short pseudohexagonal columnar crystals with a section size of 8 – 10 μm . Quartz is found in the form of fibrous formations consisting of crystals 100 – 200 μm in size which are closely cemented with the kaolinite interlayer. Besides, some fragments of the laminar kaolinite structure are randomly located over the section surface.

The mineralogical composition of the material is as follows (%): 40 – 50 quartz, 35 – 45 pyrophyllite, 5 – 15 kaolinite, 0 – 5 potassium feldspar, 0 – 10 plagioclase, 2 barite, 0.1 pyrite. The average chemical composition of the rock is as follows (%): 77.23 SiO_2 , 17.38 Al_2O_3 , 0.27 Fe_2O_3 , 0.28 CaO , 0.39 MgO , 0.35 K_2O , 0.11 Na_2O , 0.15 TiO_2 , 3.35 calcination loss. By its chemical composition (the content of chromogenic oxides) porcelain rock should be considered an alkali-free high-grade material for the porcelain industry, and by its mineralogical composition it belongs to the pyrophyllite-quartz mineral type.

Thermal and x-ray phase analysis methods revealed the phase transitions occurring in quartz-pyrophyllite rocks in heat treatment. The pyrophyllite peaks on the x-ray pattern

disappear within the temperature range of 800 – 1200°C, and lines of mullite and cristoballite appear at 1200°C. The crystalline products of the phase transitions in heating to 1450°C are quartz, mullite, and cristoballite. The intensity of the cristoballite lines on the x-ray patterns points to its relatively substantial amount. The above variations are registered on the DTA curve as endothermic effects at 375 – 450, 565 – 590, and 630 – 725°C, as well as an exothermic effect at 960 – 1010°C.

The study of the technological properties of quartz-pyrophyllite samples indicated that the process of their possible sintering occurs at relatively high temperatures. The maximal compression of the samples occurs within the temperature interval of 1400 – 1450°C with water absorption of 11.6%. The apparent density of the samples is 1.93 g/cm^3 . Judging from the results obtained, one can state that quartz-pyrophyllite material on sintering produces a material which contains the same crystalline components as cristoballite-bearing porcelain composite.

The high quartz content in the considered rock composition makes it possible to fully substitute this rock for the quartz component in porcelain mixtures, and the presence of pyrophyllite makes it possible to reduce the kaolin content in these mixtures. Taking this into account, several experimental porcelain mixture compositions were developed based on quartz pyrophyllite rocks from the Bainaksaiskoe deposit, Angrenskii secondary concentrated kaolin, Lyangarskii permattite, and Navoinskii bentonite clay. The calculated molecular composition and the acidity coefficient of the experimental porcelain materials are indicated in Table 1.

The compositions exhibit a slightly increased SiO_2 content and a low content of Al_2O_3 with respect to the classical hard porcelain composition. Therefore, the calculated values of the acidity coefficient of these mixtures are slightly higher than the soft porcelain acidity coefficients.

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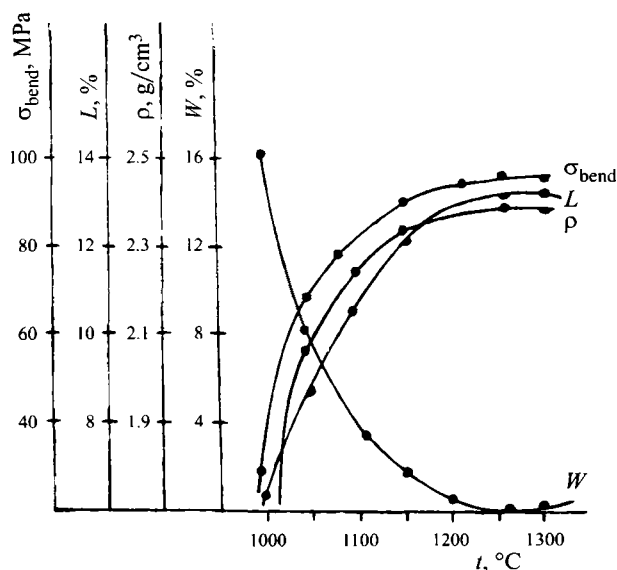


Fig. 1. Firing temperature dependence of water absorption W , density ρ , firing shrinkage L , and bending strength σ_{bend} of samples made of MT-23 mixture.

Plastically molded samples were subjected to stepwise firing at the temperature of 800–1300°C with holding for 1–2 h. The microstructure of the sintered samples was studied using a UEMB-100 B electron microscope by the direct platinum-carbon replica method.

The study of the technological and physicomachanical properties of the porcelain materials obtained revealed that the maximum shrinkage of the experimental samples is shifted toward the region of relatively low temperatures. Signs of sintering of the mixtures arise at 1100°C. The maximum compression of the samples occurs at the temperature of 1250–1300°C. The sintering interval is 220–250°C. Upon sintering at the temperature of 1300°C, samples made of the specified mixtures fully meet the requirements of GOST 28390.

The microstructure of the porcelain materials was investigated using a sample of MT-23 composition which has the optimum physicomachanical parameters. Fig. 1 shows the firing temperature dependence of the main properties of the samples made of MT-23 mixture. It should be noted that the samples fired at 1300°C exhibit sufficiently high mechanical

strength (96.0 MPa) and thermal stability (over 19 heat cycles). The whiteness degree of the samples is 66%.

The x-ray diffraction pattern of samples of MT-23 mixture after firing at the temperature of 1300°C exhibits the reflexes typical of quartz, mullite, and cristobalite. The thermogram shows an exothermic effect at 930–1000°C indicating the beginning of the formation of crystalline phases. The formation of cristobalite in porcelain is usually related to the process of vitreous phase saturation with silicic acid and conversion of part of the remaining quartz into cristobalite, which is more probable in mixtures with a high content of SiO_2 and high dispersion of the quartz component. At the same time, the cristobalite phase imparts special mechanical properties to the crock [4].

The petrographic study of MT-23 mixture fired at the temperature of 1300°C with holding for 1 h revealed the presence of a high quantity of residual quartz crystals with a grain size of 30–40 μm . Their content can attain 25%. The process of quartz grain dissolution is manifested in the form of a border 4–5 μm in size. The fine crystalline part and the tangled fibrous formations arise at the site of pyrophyllite pseudomorphoses where local circle-shaped areas filled with fibrous structural elements are found. The total amount of the vitreous mullite phase is 65–70%. The pores are mostly round, and their content attains 5%. Increasing holding of the samples at the temperature of 1300°C to 2 h results in disintegration of large crystals into smaller crystals 10–25 μm in size, and their content decreases to 15%. The small pores in this case are surrounded by a dense border. The mullite sites appear to have crystallization centers from which rays of the needle-shaped crystals depart.

The electron microscopic photos of fresh fracture of porcelain crock fired at the temperature of 1300°C with 1 h holding reveal areas with tear-shaped stratification inside the smooth glass structure in which mullite crystal formations are seen. The bulk of the vitreous phase does not have a smooth surface but appears to be covered with scaly structural elements (Fig. 2a). The photos of the samples fired at the temperature of 1300°C with 2 h holding exhibit needle-shaped mullite crystals over the entire fracture surface. Quartz crystals are observed in the dissolution stage and have a reaction border of 2–3 μm , and the needle-shaped mullite formations are the consequence of disintegration of large crystals (Fig. 2b). At the same time, the pore space of the mixture is filled with large (5–6 μm) mullite crystals

TABLE 1

Mixture	Content, mole								Acidity coefficient	$\frac{\text{R}_2\text{O}_3}{\text{R}_2\text{O} + \text{RO}}$
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2		
MT-17	21.746	3.400	0.069	0.143	0.165	0.301	0.389	0.045	1.911	3.504
MT-20	21.107	3.325	0.071	0.146	0.164	0.303	0.385	0.048	1.892	3.430
MT-23	21.424	3.393	0.068	0.145	0.163	0.303	0.388	0.047	1.887	3.495

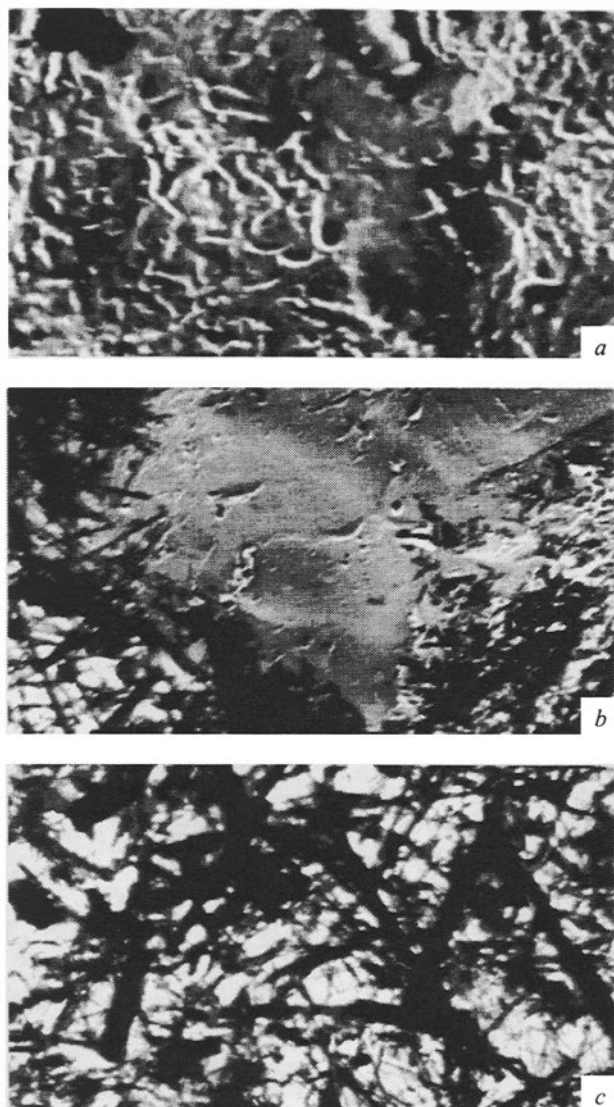


Fig. 2. Microstructure sites of porcelain made of MT-23 mixture fired at the temperature of 1300°C: a) 1 h holding ($\times 10,000$); b, c) 2 h holding ($\times 12,000$).

(Fig. 2c). The cristoballite phase is absent in the microscopic studies, which is probably related to its low content in the porcelain cakes.

It is known that the primary mullite is the product of solid-phase reactions which proceed with destruction of the metakaolinite lattice. The formation of scaly mullite proceeds via an intermediate spinel phase. However, when mullite is crystallized from dehydrated pyrophyllite, the intermediate phase is absent, and mullite is formed at once within the temperature interval of 1000–1100°C [5, 6]. Therefore, the compositions containing pyrophyllite are more favorable for mullite crystallization than the compositions with kaolinite. This is probably the reason for the predominantly scaly surface of the vitreous phase, which arises

as a consequence of incorporation of structural elements consisting of primary mullite scaly grains, which are stable in the considered temperature interval, into the vitreous phase.

The crystallization of secondary needle-shaped mullite proceeds with participation of the liquid phase and is determined by the degree of dissolution of the crystal phases in the liquid phase. The degree of quartz dissolution primarily depends on the milling dispersity and its genesis. Quartz from natural porcelain rock dissolves better than quartz sand. This is due to the fact that quartz grains under the effect of natural hydrothermal processes acquire cracks and become less strong, therefore, their reactivity increases. With an increase in the content of dissolved quartz, the amount of crystallized secondary mullite in the melt increases due to an increase in the content of vitreous phase. As a consequence, mullitization of the compositions containing quartz-pyrophyllite material proceeds actively enough at lower temperatures.

The tear-shaped areas registered in the microscopic photos are apparently the reflection of microheterogeneous areas arising due to the melt saturation by basic or acid components. In this case, mullite crystallization in the form of fibrous formations begins with the local areas mostly saturated by alumina.

The formation of cristobalite in the investigated mixture is probably largely caused by quartz from natural porcelain rock. The residual quartz grains from quartz-pyrophyllite material, as well as the quartz formed upon conversion of pyrophyllite to mullite can recrystallize as cristobalite, which imparts good mechanical properties to the porcelain material.

Thus, quartz-pyrophyllite material has a favorable effect on the physicochemical processes in firing of mixtures and facilitates the earlier aging of porcelain crock and crystallization of cristobalite in addition to mullite. Porcelain structure formation in this case is accompanied by intense evolution of both scaly and needle-shaped mullite. The vitreous phase, the primary and secondary mullite crystals, the residual quartz grains, and the cristobalite phase impart good physicomachanical properties to porcelain material.

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